Journal of Photochemistry and Photobiology A: Chemistry 201 (2009) 208–213

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

# Excited-states and lightfastness of linear *trans*-quinacridone pigment nanoparticles

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ARTICLE INFO

*Article history:*
Received 1 August 2008
Received in revised form 17 October 2008
Accepted 29 October 2008
Available online 19 November 2008

*Keywords:*
Linear *trans*-quinacridone
Lightfastness
Organic nanoparticle
Reprecipitation method

ABSTRACT

The photoexcited state of linear *trans*-quinacridone pigment nanoparticles, prepared by a reprecipitation method, was analyzed by time-resolved spectroscopy. The analysis showed that the $S_1$ state of the linear *trans*-quinacridone nanoparticles undergoes a quantitative, non-radiative relaxation to the ground state with a time constant of about 100 ps. By contrast, the $S_1$ state of the molecular dispersion state (dilute solution state) was relatively long-lived (21 ns). This, together with the intersystem crossing to $T_1$ observed in the molecular dispersion state, clearly distinguished the nanoparticles from the molecular dispersion state. By comparing the two in terms of lightfastness, the nanoparticles were found to be much more lightfast than the molecular dispersion state. It was speculated that the superior lightfastness of the linear *trans*-quinacridone pigment nanoparticles was not due to the molecular structure but the facilitated $S_1$ relaxation by the aggregation of the molecules.

## 1. Introduction

As a high-performance organic pigment having excellent color reproducibility, heat resistance, and lightfastness, the linear *trans*-quinacridone has been used in a wide range of applications, such as paints, printing, and ink for ink-jet printers [1]. Recently, the linear *trans*-quinacridone has gained a great deal of attention and various studies are underway to explore its potential use as a functional material in the fields of, for example, organic EL [2] and organic thin-film solar cells [3]. Currently, the linear *trans*-quinacridone is used as an amorphous thin-film, formed by vacuum deposition method, or in the form of pigment particles having a particle size of about 100 nm or greater. It is expected that the linear *trans*-quinacridone, with a reduced particle size of about 20 nm, would provide a new kind of functional nanomaterial, free from the influence of light scattering. As a specific example of such an application, a report is presented of an attempt to use the pigment nanoparticles for the color filter of liquid crystal displays [4].

Generally, pigments are more lightfast than dyes; however, it is known that the lightfastness deteriorates when the pigments are turned into fine particles [1]. It is therefore very meaningful to elucidate the relationship between the photoexcited state and lightfastness, in order to put the pigment nanoparticles in practical applications.

In contrast to many detailed studies made on polymorphism [5] and electrical properties [6] of the linear *trans*-quinacridone pigment, only a few reports are available that deal with the dynamics of photoexcited state. To our knowledge, the studies on linear *trans*-quinacridone vapor-deposited film (Rossi et al.) [7–9] are practically the only reports available on this subject. One of the factors for this lack of research is the difficulties in analyzing the solid sample, like a pigment powder, by ultrafast time-resolved spectrometry. As a technique to analyze the photoexcited state of the solid powder, there have been reports of a technique using a dispersion liquid of nanoparticles, prepared by a reprecipitation method devised as a method of preparing organic nanoparticles [10]. The technique has proved convenient for realizing time-resolved spectrometry for solid samples such as polydiacetylene nanoparticles [11], or dye-containing oil droplet of color paper [12], for example. In this paper, we report the result of examination on the relationship between the dynamics of photoexcited state and lightfastness, concerning optically transparent, dispersion-stable linear *trans*-quinacridone nanoparticles prepared by the reprecipitation method.

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doi:10.1016/j.jphotochem.2008.10.024

## 2. Experimental

### 2.1. Samples

Linear *trans*-quinacridone purified by sublimation was purchased from Tokyo Chemical Industry Co., Ltd., and was directly used without further purification. The guaranteed reagents, dimethyl sulfoxide (DMSO) and *N*-methyl-2-pyrrolidinone (NMP), available from Wako Pure Chemical Industries, Ltd., were used as good solvents required for the preparation of the organic nanoparticles by the reprecipitation method. As a poor solvent, ultrapure water (18 MΩ cm), prepared by using an ultrapure water production unit Milli-Q Advantage (Millipore) was used.

### 2.2. Preparation of linear trans-quinacridone nanoparticles

A dispersion liquid of linear *trans*-quinacridone nanoparticles was typically prepared through reprecipitation method by the following procedure. The linear *trans*-quinacridone was dissolved in the good solvent NMP to make the concentration 1 mM. Two hundred microliters of the solution was injected into 10 mL of vigorously stirred ultrapure water (controlled at 20 °C) using a microsyringe, so as to prepare a nanopigment dispersion liquid. For the rest of the procedure, we followed the preparation method described in detail in the Refs. [10,13].

### 2.3. Spectroscopic study

Measurement of the electronic absorption spectrum was performed using a spectrometer UVPC-2400 (Shimadzu). The fluorescence spectrum was measured using a photon-counting fluorescence spectrometer, Fluololog 3 (Horiba), under no influence of resorption by adjusting the optical density of the sample to 0.2–0.3. Measurement of fluorescence quantum yield was made using an absolute quantum yield measurement system C9920-2 (Hamamatsu Photonics K.K.). The optical density and other sample conditions were the same as in the fluorescence measurement. Measurement of fluorescence lifetime was performed with a system using a semiconductor laser SLDH-041 (wavelength 405 nm, pulse width 50 ps; Hamamatsu Photonics K.K.) as the excitation light source, and a streak camera C-4337 (Hamamatsu Photonics K.K.) as a detector. Time-resolved thermal lens measurement was performed using a system (Unisoku Co., Ltd.) in which a nanosecond YAG laser SLII-10 and a SLOPO wavelength conversion unit (both available from Continuum) were used as the excitation light source. CVI Melles Griot's He–Ne laser (632.8 nm, 1 mW) was used as the probe laser. The probe light was so focused as to have a spot diameter of about 0.1 mm on the sample surface; and the light intensity change through the pinhole having a diameter of 0.4 mm, as disposed between the sample and the detector, was detected for time resolution. The sample was degassed by argon bubbling. For quantitative discussion, the sample must be analyzed in a region free from excitation light intensity dependency on thermal lens signals. The excitation light intensity was gradually lowered from 100 μW, and the sample was analyzed at 5–10 μW at which it was free from intensity dependency. Measurement of the emission spectrum in the near-infrared region, such as the emission detection of singlet oxygen was performed with a system (Ritsu) using a xenon lamp MAXCUTE 302 (Asahi Spectra Co., Ltd.) as the light source, and a Ge detector EO-817L (North Coast Scientific). For kinetic study of pigment's excited states, we built a sub-picosecond dynamics measurement system. This system is provided with wavelength-tunable excitation light and the time resolution of our system is 100 fs, and the lower limit of detection is $1 \times 10^{-5}$ AU.

### 2.4. Characterization of linear trans-quinacridone nanoparticles

For the size and distribution measurement of the nanoparticles in the dispersion liquid, a dynamic light scattering analyzer LB-550 (Horiba) was used. Measurement of primary particle size was made through observation of the nanoparticles after filtration with a Millipore filter, using a scanning electron microscope S-5500 (Hitachi). As a pretreatment to avoid electrification, Os was vapor-deposited on the sample to form a film having a thickness of 1–2 nm. The zeta potential of the nanopigment was measured using a zeta potential measurement device NANO-ZS (Sysmex). The crystal form of the linear *trans*-quinacridone nanoparticles prepared by the reprecipitation method was identified from the peak positions of the powder X-ray diffraction pattern measured by an X-ray diffractometer RIN 2500 (Rigaku).

Evaluation of lightfastness of the nanoparticles was made using a merry-go-round lightfastness tester (Eagle Engineering) equipped with a 500 W xenon lamp as the light source. To avoid influence of heat, a heat absorbing filter HA-50 (Hoya Candeo Optronics Corporation) was inserted between the light source and sample. The illuminance at a sample surface was 120,000 lx. The lightfastness evaluation is as follows: the absorbance at the absorption maximum of the sample relative to the light irradiation time was measured, and the ratio of the absorbance at each irradiation time to the absorbance before light irradiation (defined as residual ratio) was computed.

## 3. Results and discussion

### 3.1. Characterization of linear trans-quinacridone nanoparticles

Fig. 1 shows the structural formula of the linear *trans*-quinacridone, together with an example of a dispersion liquid of linear *trans*-quinacridone nanoparticles prepared by the reprecipitation method. The dispersion liquid of nanoparticles was almost free from the influence of light scattering, and was optically transparent to such an extent that it was almost indistinguishable from the dilute solution by visual inspection. Further, the dispersion liquid was stable without any addition of dispersant such as a surfactant, making the liquid suitable for various kinds of spectroscopy. Presumably, the high dispersion stability has something to do with the relatively high zeta potential of −35 mV. Though the factors responsible for the relatively high zeta potential of the nanoparticles prepared by the reprecipitation method are unclear,

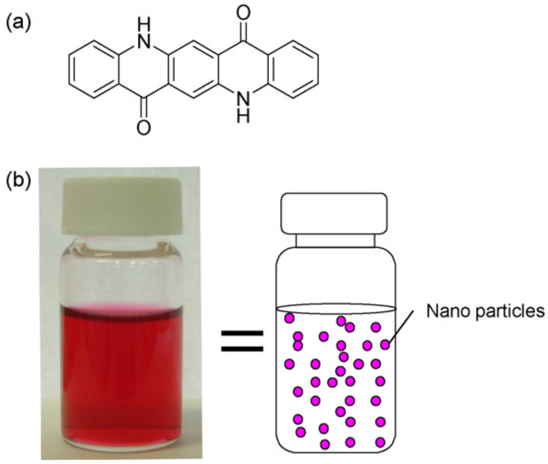

**Fig. 1.** (a) Structure of linear *trans*-quinacridone. (b) Photograph of dispersion liquid of the nanoparticles comprising linear *trans*-quinacridone prepared by reprecipitation method and schematic illustration of dispersion liquid.

involvement of static electricity generated by the friction between the nanoparticle surface and the poor solvent is suspected [14].

Fig. 2 shows a scanning electron micrograph (SEM image) of the linear *trans*-quinacridone nanoparticles. The SEM image confirmed formation of highly monodispersive nanoparticles having a particle size of about 20 nm. The value obtained from the SEM image substantially coincided with the number average particle size of 22.5 nm determined by a dynamic light scattering method. It became clear from this that the linear *trans*-quinacridone nanoparticles exist as the dispersion of non-aggregate primary particles in the dispersion liquid.

It is known that the linear *trans*-quinacridone pigment has crystal polymorphism, including α, β, and γ forms. From the measurement of the powder X-ray diffraction pattern of the linear *trans*-quinacridone nanopigment prepared by the reprecipitation method, the linear *trans*-quinacridone pigment was found to be of α form, by comparison of the peak positions with those of Ref. [15].

### 3.2. Excited-states of linear trans-quinacridone nanoparticles

#### 3.2.1. Absorption and fluorescence spectra

The electronic absorption spectrum and fluorescence spectrum of the nanoparticle dispersion liquid of linear *trans*-quinacridone are shown in Fig. 3. Since slight dissolution of the linear *trans*-quinacridone in NMP or DMSO is possible, the spectra of the molecular dispersion state (dilute solution) are also shown for comparison. As previously reported [13], a red-shift was observed in the electronic absorption spectrum of the nanoparticles, as compared with the molecular dispersion state. The molar absorptivities of the nanoparticles and the molecular dispersion state were 5200 cm $M^{-1}$ (520 nm) and 13,220 cm $M^{-1}$ (524 nm), respectively. While no fluorescence was observed from the nanoparticles (quantum yield ($\Phi_{fl}$) < $10^{-4}$), the molecular dispersion state had a fluorescence spectrum that was a mirror-image of the electronic absorption spectrum. The fluorescence quantum yield was $\Phi_{fl}$ = 0.76 (in DMSO). The regression of the fluorescence decay could occur single-exponentially. The fluorescence lifetime was 21.4 ns. This value coincided with the fluorescence lifetime (20 ns) of the previously reported linear *trans*-quinacridone derivative solubilized by *N*-alkylation [16].

#### 3.2.2. Time-resolved thermal lens spectrometry

To further clarify the dynamics of the excited states of the nanoparticles and the molecular dispersion state, analysis was made using a time-resolved thermal lens method (TRTL). The thermal lens method is a technique that allows for a quantitative analysis of the relaxation process involving no emission. By the time-resolved measurement of thermal lens signals, the relaxation from the lowest excited singlet state ($S_1$) and the relaxation from the lowest excited triplet state ($T_1$) can be distinguished from each other, and the quantum yield by the $S_1$ to $T_1$ intersystem crossing can be estimated. In other words, in the absence of fluorescence as in the nanoparticle dispersion liquid, one can clearly distinguish whether the transition is the non-radiative relaxation from $S_1$, or the intersystem crossing from $S_1$ to $T_1$.

Fig. 4 shows time-resolved thermal lens signals from the nanoparticle dispersion liquid and the dilute solution. From the nanoparticles, only the fast component ($U_f$), rising within the pulse width of the nanosecond laser was observed, and the slow component ($U_s$) was not observed. It was inferred from this that the nanoparticles undergo a quantitative thermal relaxation from the

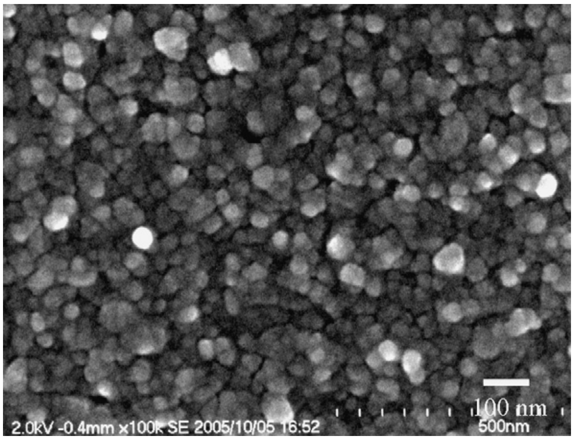

**Fig. 2.** SEM image of linear *trans*-quinacridone nanoparticles prepared by reprecipitation method.

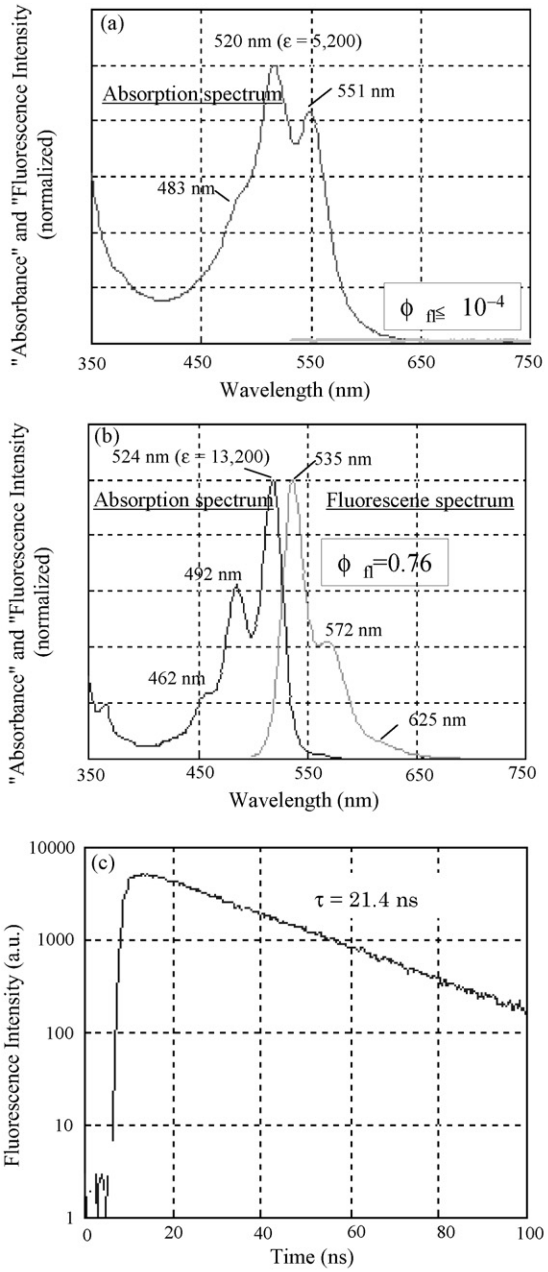

**Fig. 3.** Absorption- and fluorescence spectra of linear *trans*-quinacridone, (a) dispersion liquid of the nanoparticles and (b) molecular dispersion (dilute solution). (c) Fluorescence decay of the linear *trans*-quinacridone molecular dispersion.

$S_1$ state to the ground state ($S_0$). By contrast, the molecular dispersion state had the slow component ($U_s$), in addition to the fast component ($U_f$) within the nanosecond pulse width. These results indicate the occurrence of the intersystem crossing from $S_1$ to $T_1$ in the molecular dispersion state [17]. The quantum yield of the intersystem crossing was estimated as 0.23.

### 3.2.3. Generation of singlet oxygen

Consideration to the singlet oxygen is very important in discussing the lightfastness of the functional organic materials. Because of the $S_1$ to $T_1$ intersystem crossing, the linear *trans*-quinacridone molecular dispersion state has a possibility of generating singlet oxygen. To access this, we attempted emission detection of singlet oxygen in the near-infrared emission region (1270 nm). The test did not detect any singlet oxygen emission with the DMSO solvent used in the TRTL method; however, it detected singlet oxygen-derived emission with an emission maximum at 1270 nm, when the solvent was a mixed solvent of chloroform ($CHCl_3$) [18] and DMSO providing a relatively longer lifetime for the singlet oxygen, as shown in Fig. 5. It became clear from this that the molecular dispersion state generates singlet oxygen by self-sensitizing $^1O_2$ reaction. By contrast, no singlet oxygen was detected from the nanoparticles, in which no $T_1$ intersystem crossing occurs.

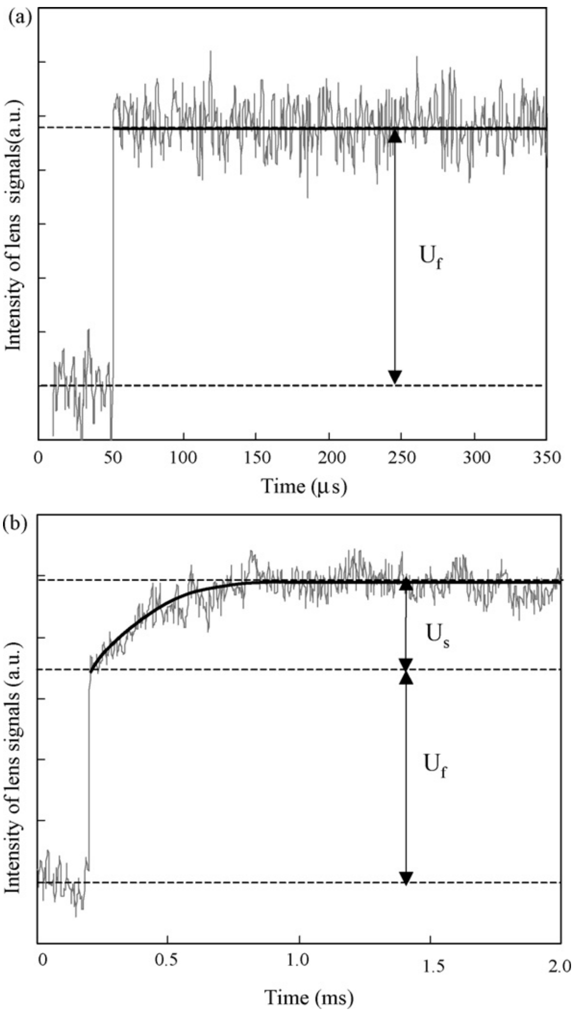

**Fig. 4.** Time-resolved thermal lens signal of linear *trans*-quinacridone, (a) dispersion liquid of the nanoparticles and (b) linear *trans*-quinacridone (dilute solution). The excitation wavelength was 520 nm (0.2 mW) and 524 nm, respectively. Samples ware deaerated before analysis.

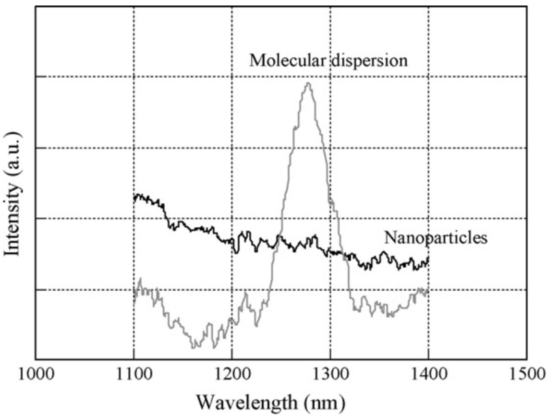

**Fig. 5.** Emission of singlet oxygen generated by energy transfer from linear *trans*-quinacridone.

### 3.2.4. Transient absorption spectra

In the linear *trans*-quinacridone nanoparticles, information concerning dynamics of $S_1$ cannot be obtained from the fluorescence, because the relaxation from $S_1$ to the ground state occurs by the quantitative, non-radiative process. In an attempt to overcome this, we analyzed the dynamics of the $S_1$ state by measuring the $S_1$–$S_n$ absorption in the nanoparticles, using an time-resolved spectroscopy system equipped with a wavelength-variable femtosecond laser as the excitation light source (produced by us for this purpose). This system had the time resolution of 100 fs, and a lower detection limit of $1 \times 10^{-5}$ AU, both of which are sufficient for the measurement of $S_1$–$S_n$ absorption [12].

In analyzing the dynamics of a high-density aggregation system such as the linear *trans*-quinacridone nanoparticles, care must be taken for the relaxation process between excitons, such as $S_1$–$S_1$ annihilation. Before performing an time-resolved measurement using a pump-probe method, dependence of transient response on pump light intensity was examined. When the pump light intensity was gradually decreased from 2 mW, the time constant of the transient response leveled off at or below 0.2 mW. Based on this, we measured the dynamics of the nanoparticles at a pump light intensity of 0.2 mW.

Fig. 6 shows a time-varying transient absorption spectrum and a transient response of the nanoparticle dispersion liquid. Immediately after excitation, shown in Fig. 6(a), a bleach was observed near 475–560 nm, corresponding to the electronic absorption spectrum, and transient absorption was observed near 600–750, and 405–450 nm. In the transient absorption near 405–420 nm, shown in Fig. 6(b), a rise with a time constant of 0.3 ps was observed. It was found that the bleach near 513–524 nm undergoes a relaxation to the ground state at time constants of 0.3, 10, and 110 ps (the data of 110 ps slow component is omitted). The 0.3 ps fast component corresponded to the rise of transient absorption at 405–420 nm. From these observations, we speculated that this was attributed to the relaxation process from the metastable state to the stable state immediately after excitation. The 10 and 110 ps components were attributed to the relaxation process to the ground state. A close look at the transient absorption spectrum near 600–750 nm reveals changes in waveform over time near 590, and 670–710 nm. It was inferred from this that the transient absorption spectrum in this region was an overlap of multiple components. As described above, the $S_1$ state of the molecular dispersion state component is relatively long-lived (21.4 ns), and it partially undergoes intersystem crossing to $T_1$. This is in clear contrast to the $S_1$ state of the nanoparticles, which underwent a non-radiative relaxation to the ground state in a very short time period.

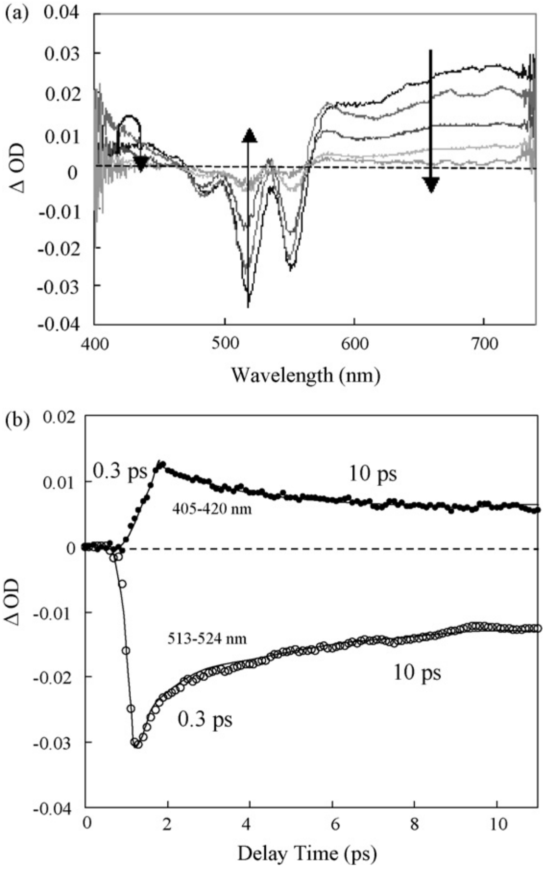

**Fig. 6.** (a) Time-resolved transient absorption spectra of linear *trans*-quinacridone nanoparticles measured with our sub-picosecond dynamics measurement system. The excitation wavelength was 520 nm (0.2 mW). Delay times are 0.2, 1.0, 10, 100, 600 ps, respectively. (b) Transient response of $S_1$ state of linear *trans*-quinacridone nanoparticles. 513–524 nm; open circle, 405–420 nm; closed circle.

### 3.2.5. Excited state dynamics of linear trans-quinacridone

From these results, schematically summarizes the dynamics of the photoexcited states of the nanoparticles and molecular dispersion state of the linear *trans*-quinacridone. It was speculated that the nanoparticles undergoes a relaxation from the metastable to stable state at the time constant of 0.3 ps after photoexcitation, followed by a substantially quantitative relaxation to the ground state at the time constants of 10 and 110 ps. In contrast, the molecular dispersion state was shown to have a relatively long $S_1$ lifetime (21.4 ns), emit fluorescence with a quantum yield of 0.74, and undergo intersystem crossing to $T_1$ state. The $S_1$ state of the nanoparticles was found to be very short-lived, at most 1/200 of the $S_1$ lifetime of the molecular dispersion state. We speculate that this is due to the vibrational relaxation by the interaction of the molecules in the nanoparticles. Detailed studies are underway to provide more precise explanations.

### 3.3. Lightfastness of linear trans-quinacridone nanoparticles

Fig. 7 shows the results of evaluation regarding the lightfastness of the linear *trans*-quinacridone, between the nanoparticle dispersion liquid and the dilute solution (molecular dispersion state form). Within the time frame of this study, almost no photodegradation occurred in the nanoparticles. The molecular dispersion state, in contrast, had considerably lower lightfastness than the nanoparticles. As described, the molecular dispersion state generates singlet oxygen, which leads us to think that the photofading is primarily due to the self-sensitizing singlet oxygen oxidation reaction. In contrast, such photofading reaction appears to be unlikely in the nanoparticles, which, unlike the molecular dispersion state, undergo a non-radiative relaxation from the $S_1$ state to the ground state in a very short time period. We estimated that the rapid relaxation of the excitation state is the essential factor for the high-level lightfastness of pigment nanoparticles. Presumably, the fact that the most of the molecules are inside the nanoparticles where they do not interact with oxygen enhances the high-level lightfastness of the nanoparticles.

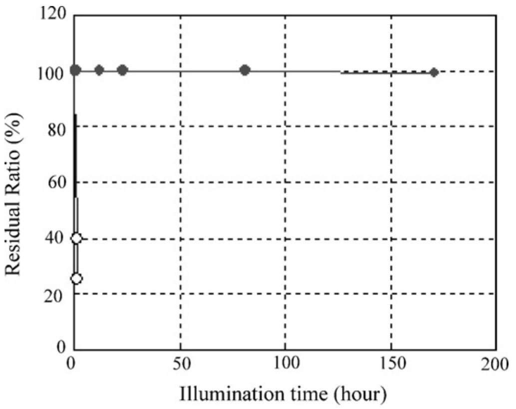

**Fig. 7.** Lightfastness of linear *trans*-quinacridone nanoparticles (closed circle) and molecular dispersion (open circle).

Considering these results in terms of the dynamics of the photoexcited state, we estimate that the good lightfastness of the nanoparticles and pigment of the linear *trans*-quinacridone are not due to the molecular structure itself but the vibrational relaxation from the $S_1$ state to the ground state, which is facilitated by the aggregation structure of the particles.

We are now testing their practical advantages and their superior durability against light irradiation compared with amorphous film and larger pigment particles. We would like to publish these results in the near future.

## 4. Conclusion

The photoexcited state of linear *trans*-quinacridone pigment nanoparticles prepared by the reprecipitation method was analyzed to elucidate its dynamics. The result showed that the pigment nanoparticles, unlike the molecular dispersion state form, are very likely to undergo a relaxation from the excited state. Presumably, the superior lightfastness of the linear *trans*-quinacridone pigment nanoparticles is not due to the molecular structure but, to a large part, the relaxation of the $S_1$ state facilitated by the aggregation of the molecules.

## Acknowledgments

This work is financially supported by New Energy and Industrial Development Organization, Japan. The authors wish to thank Mr. Shinichi Horino and Ms. Keiko Mesaki for their assistance in performing various experiments, and to express our sincere gratitude to Professor Hidetoshi Oikawa and many students of Oikawa Laboratory for preparation of nanoparticles by reprecipitation method.

## References

[1] W. Herbst, K. Hunger, Industrial Organic Pigments: Production, Properties, Applications (3rd, Completely Revised Edition), Wiley–VCH, 2004.
[2] T. Tsutsui, E. Aminaka, Y. Fujita, Y. Hamada, S. Saito, Synth. Met. 57 (1993) 4157.
[3] M. Tomida, S. Kusabayashi, M. Yokoyama, Chem. Lett. (1984) 315.
[4] Y. Miyashita, K. Baba, H.Kasai, H. Nakanishi, T. Miyashita, Mol. Cryst. Liq. Cryst., 492 (2008), 268[632].

[5] G. Lincke, Dyes Pigments 44 (2000) 101.
[6] J. Kalinowski, W. Stampor, P. Di Marco, V. Fattori, Chem. Phys. 182 (1994) 341.
[7] L. Rossi, G. Bonginovanni, G. Lanzani, A. Mura, A. Borghesi, R. Tubino, J. Kalinowski, Adv. Mater. Opt. Electron. 7 (1997) 83.
[8] L. Rossi, G. Bonginovanni, J. Kalinowski, G. Lanzani, A. Mura, M. Nisoli, R. Tubino, Chem. Phys. Lett. 257 (1996) 545.
[9] L. Rossi, G. Bonginovanni, A. Borghesi, G. Lanzani, J. Kalinowski, A. Mura, R. Tubino, Synth. Met. 84 (1997) 873.
[10] H. Kasai, H.S. Nalwa, H. Oikawa, S. Okada, H. Matsuda, N. Minami, A. Kakuta, K. Ono, A. Mukoh, H. Nakanishi, Jpn. J. Appl. Phys. 31 (1992) L1132.
[11] T. Asahi, K. Kibisaki, H. Masuhara, H. Kasai, H. Katagi, H. Oikawa, H. Nakanishi, Mol. Cryst. Liq. Cryst. 314 (1998) 95.
[12] Y. Miyashita, J. Mori, H. Yokoyama, M. Yoshikane, H. Watanabe, K. Takeuchi, H. Kasai, H. Nakanishi, T. Miyashita, J. Photochem. Photobiol. A: Chem. 194 (2008) 129.
[13] K. Ujiie-Ishii, K. Baba, Z. Way, H. Kasai, H. Nakanishi, S. Okada, H. Oikawa, Mol. Cryst. Liq. Cryst. 445 (2006), 177[467].
[14] M. Chikazawa, K. Tajima, Kaimenkagaku (Surface Science), MARUZEN Co., Ltd., 2001, Chap. 2 (in Japanese).
[15] D.S. Filho, C.M. Oliveira, J. Mater. Sci. 27 (1992) 5101.
[16] P.-H. Liu, H. Tian, C.-P. Chang, J. Photochem. Photobiol. A: Chem. 137 (2000) 99.
[17] F. Tanaka, T. Furuta, M. Okamoto, S. Hirayama, Phys. Chem. Chem. Phys. 6 (2004) 1219.
[18] N.J. Turro, Modern Molecular Photochemistry, The Benjamin/Cummings Publishing Company, MemloPark, CA, 1978 (Chap. 14).